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Seasonal variations and source estimation of saccharides in atmospheric particulate matter in Beijing, China

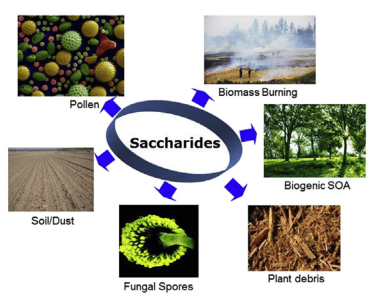
Linlin Liang [a, b, *], Guenter Engling [c, d], Zhenyu Du [b, e], Yuan Cheng [b], Fengkui Duan [b], Xuyan Liu [b, f], Kebin He [b, **]

[a] State Key Laboratory of Severe Weather, Key Laboratory for Atmospheric Chemistry, Chinese Academy of Meteorological Sciences, Beijing, China
[b] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, China
[c] Department of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, Hsinchu, Taiwan
[d] Division of Atmospheric Sciences, Desert Research Institute, Reno, NV, USA
[e] National Research Center for Environmental Analyses and Measurements, Beijing, China
[f] National Satellite Meteorological Center, China Meteorological Administration, Beijing, China

HIGHLIGHTS

- Total measured saccharide concentrations in $PM_{2.5}$ and PM_{10} were higher than most of those observed around the world.
- The ratio of levoglucosan to mannosan was higher during the harvest season.
- Ambient sugars and sugar alcohols were more abundant in fine mode ($PM_{2.5}$) during winter.
- Saccharides in Beijing aerosol can be derived from biomass burning, suspended soil, isoprene SOA, fungal spores and pollen.

GRAPHICAL ABSTRACT



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ABSTRACT

Saccharides are important constituents of atmospheric particulate matter (PM). In order to better understand the sources and seasonal variations of saccharides in aerosols in Beijing, China, saccharide composition was measured in ambient PM samples collected at an urban site in Beijing. The highest concentrations of total saccharides in Beijing were observed in autumn, while an episode with abnormal high total saccharide levels was observed from 15 to 23 June, 2011, due to extensive agricultural residue burning in northern China during the wheat harvest season. Compared to the other two categories of saccharides, sugars and sugar alcohols, anhydrosugars were the predominant saccharide group, indicating that biomass burning contributions to Beijing urban aerosol were significant. Ambient sugar and sugar alcohol levels in summer and autumn were higher than those in spring and winter, while they were more abundant in $PM_{2.5}$ during winter time. Levoglucosan was the most abundant saccharide compound in both $PM_{2.5}$ and PM_{10}, the annual contributions of which to total measured saccharides in $PM_{2.5}$ and PM_{10} were 61.5% and 54.1%, respectively. To further investigate the sources of the saccharides in ambient aerosols in Beijing, the PM_{10} datasets were subjected to positive matrix factorization (PMF) analysis. Based on the

* Corresponding author. State Key Laboratory of Severe Weather, Key Laboratory for Atmospheric Chemistry, Chinese Academy of Meteorological Sciences, Beijing, China.
** Corresponding author. State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, China
E-mail addresses: liangll2014@camscma.cn (L. Liang), hekb@tsinghua.edu.cn (K. He).

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Emission sources
Beijing

objective function to be minimized and the interpretable factors identified by PMF, six factors appeared to be optimal as to the probable origin of saccharides in the atmosphere in Beijing, including biomass burning, soil or dust, isoprene SOA and the direct release of airborne fungal spores and pollen.

1. Introduction

Saccharides, the major class of water-soluble organic compounds (WSOC), constitute important components of ambient aerosols over continental (Graham et al., 2003; Yttri et al., 2007; Fu et al., 2012; Jia and Fraser, 2011), marine (Simoneit et al., 2004), and high Arctic regions (Fu et al., 2009). Saccharides have been reported to account for 13–26% of the total organic compound mass identified in continental aerosols, and as much as 63% in oceanic aerosols (Simoneit et al., 2004). Selected saccharides in atmospheric aerosols have been proposed as tracers for the sources, processes and transport of biologically important organic material in the natural environment (Simoneit et al., 2004; Liang et al., 2013; Choi et al., 2015). Various studies have identified saccharides to be emitted from biomass burning (e.g., Wang et al., 2011; Ho et al., 2014), suspended soil or dust (Simoneit et al., 2004; Rogge et al., 1993; Fu et al., 2012), and associated with primary biological aerosol particles (Bauer et al., 2008; Elbert et al., 2007; Graham et al., 2003; Liang et al., 2013; Zhu et al., 2015).

Emissions from biomass burning activities have been investigated with anhydrosugars, synonymous with anhydrous saccharides or monosaccharide anhydrides. Anhydrous saccharides, including levoglucosan, mannosan and galactosan, are generated during pyrolysis of cellulose and hemicellulose (Simoneit et al., 1999; Du et al., 2015). Levoglucosan, the most abundant species in biomass smoke particles, has been recognized as a key tracer of biomass burning emissions (Simoneit et al., 1999; Fraser and Lakshmanan, 2000; Ho et al., 2014). Moreover, levoglucosan has been tested and confirmed for assessment of long-range transport of biomass burning source emissions (Fraser and Lakshmanan, 2000; Mochida et al., 2010). However, recent laboratory studies found that the degradation of levoglucosan by OH is prominent during air mass aging (e.g., Lai et al., 2014). On regional scale, Mochida et al. (2010) observed a significant decay of levoglucosan in summer after long-range transport. Therefore, it is important to pay attention to the uncertainty when conducting source apportionment studies based on molecular tracers if the extent of degradation of levoglucosan concentrations is not considered in source apportionment models (Sang et al., 2013).

Soil or mineral dust can be resuspended by wind or agricultural practices and consequently contribute to ambient aerosols (Ma et al., 2009; Simoneit et al., 2004). Saccharide compounds measured in this emission category include a variety of sugars and sugar alcohols, among which glucose, fructose, and trehalose (also called mycose) were proposed as marker compounds for soils from five types of crop fields in the San Joaquin Valley of California (Rogge et al., 2007).

Primary biological aerosol particles (PBAPs), are another important source for saccharides in ambient aerosol; PBAPs are biologically derived material such as fungal spores, pollens, bacteria, fragments of plants and animals (Jaenicke, 2005; Jaenicke et al., 2007; Elbert et al., 2007; Despres et al., 2012). For example, a higher contribution of PBAP tracers to WSOC was found in summer (14.9%) at Cape Hedo, Okinawa Island, Japan (Zhu et al., 2015). Womiloju et al. (2003) reported that airborne pollen and fungal spores contribute 12–22% to the total organic carbon of some ambient aerosols. Jaenicke (2005) showed that primary biogenic aerosols (including plant fragments, pollen, etc.) can comprise from 20 to 30% of the total atmospheric PM (>0.2 μm) from Lake Baikal (Russia) and Mainz (Germany). Sadys et al. (2014) observed that *Ganoderma* sp. spores in England were transported over a long distance (200 km) from a forest. However, the importance of PBAPs in atmospheric PM is still not given adequate attention (Hoffmann and Warnke, 2007).

Saccharides have been detected in aerosols in a wide variety of regions by different research groups (e.g., Simoneit et al., 2004; Carvalho et al., 2003; Yttri et al., 2007), with the observed sugar species spanning a large range in ambient concentrations among these studies; for instance, 141–311 ng m^{-3} for the sum of total sugar species detected at urban and suburban sites (Yttri et al., 2007), 1.6–180 ng m^{-3} at forested sites (Carvalho et al., 2003), 9.9–455 ng m^{-3} at rural and agricultural sites (Carvalho et al., 2003; Yttri et al., 2007), and 0.28–12.5 μg m^{-3} in a agro-industrial region in India (Scaramboni et al., 2015). The atmospheric concentration levels, size distributions, seasonal and spatial distributions and source strength of the sugars, however, have not yet been sufficiently examined, particularly in East Asia. In light of the limited number of studies on quantifying the contributions of soil and PBAPs to ambient aerosol, there is an important need to characterize biologically derived PM sources, especially in regions where the role of agricultural and natural sources is greater than more traditional urban sources such as mobile sources.

Particular attention has been paid to atmospheric chemical studies in Beijing, China, because of the significant anthropogenic emissions of gaseous pollutants and aerosols in this region due to the rapid increase of industrialization (Huebert et al., 2003). Thus, most of the air pollution studies in Beijing have focused on both inorganic and organic components of aerosols associated with anthropogenic sources (Li et al., 2013), while little research was focused on biogenic emissions among the massive aerosol burden in Beijing. Our former research has revealed that fungal spores (i.e., one kind of PBAP) in Beijing were present at concentration levels which were noticeably higher than those in urban areas in Europe (Liang et al., 2013). Moreover, ambient concentrations of 2-methyltetrols, representing an important class of biogenic secondary organic aerosol (SOA), also are comparable with those in European and American cities (Liang et al., 2012; Yttri et al., 2007; Jia et al., 2010). Nevertheless, there is little known about the molecular and seasonal distribution of atmospheric saccharides and their contribution to the serious haze in this region.

In light of these research gaps, this study was conducted to investigate the role of aerosol saccharides as indicators of major aerosol sources, as well as to describe the atmospheric concentration levels, seasonal variation and the probable sources of saccharides in $PM_{2.5}$ and PM_{10} at an urban site in Beijing, China.

2. Experimental section

2.1. Sample collection

Aerosol samples were collected on the campus of Tsinghua University (THU), located in an urban area of Beijing, which has been described elsewhere (He et al., 2001; Jia et al., 2008). Daily PM_{10} and $PM_{2.5}$ samples were collected simultaneously at the THU